Applications of Silicon Carbide for High Temperature Electronics and Sensors

Virgil B. Shields

Present Address: Jet Propulsion Laboratory, California Institute of Technology, MS 303-308, 4800 Oak Grove Drive, Pasadena, California 91109, USA

ABSTRACT

Silicon carbide (SiC) is a wide bandgap material that shows great promise in highpower and high temperature electronics applications because of its high thermal conductivity and high breakdown electrical field. The excellent physical and electronic properties of SiC allows the fabrication of devices that can operate at higher temperatures and power levels than devices produced from either silicon or GaAs. Although modern electronics depends primarily upon silicon based devices, this material is not capable of handling many special requirements. Devices which operate at high speeds, at high power levels and are to be used in extreme environments at high temperatures and high radiation levels need other materials with wider bandgaps than that of silicon. Many space and terrestrial applications also have a requirement for wide bandgap materials. SiC also has great potential for high power and frequency operation due to a high saturated drift velocity. The wide bandgap allows for unique optoelectronic applications, that include blue light emitting diodes and ultraviolet photodetectors. New areas involving gas sensing and telecommunications offer significant promise. Overall, the properties of SiC make it one of the best prospects for extending the capabilities and operational regimes of the current semiconductor device technology.

INTRODUCTION

Silicon Carbide (SiC) is a wide bandgap semiconductor (2.3 -3.3 eV) that exists in a wide variety of crystal structures. SiC was one of the first semiconductor materials that was investigated for use in practical electronics applications. This material first attracted wide attention following the initial crystal growth experiments of J. A. Lely in Germany in 1955 that provided the first process for growing very pure SiC crystals [1]. The importance of SiC is based upon its durability and potential use at high temperature (>300°C) and power levels, and in elevated radiation environments. The high value of the low field mobility, electrical breakdown field, and thermal conductivity of silicon carbide results in a high figure of merit for microwave devices that could be constructed from this material. In addition, silicon carbide as a refractory material, is well-known for its chemical stability and mechanical hardness. Of all the wide bandgap materials considered for electronic applications, SiC is the most developed.

initial interest in SiC for semiconductor applications resulted from requirements for high temperature, corrosion resistant materials. Advances in micro device processing in addition to a need for higher operating frequencies, greater power handling capabilities, and increased device packaging densities have spurred the present developments in SiC material and device technologies. The progress in bulk and epitaxial growth technologies over the last decade have been the key to SiC's achieving its present dominance in the wide bandgap material arena. Although the material quality still requires improvement, a considerable amount of research effort is focused on solving those problems in commercial, university, and government laboratories around the world.

SIC PROPERTIES AND CHARACTERISTICS

Table 1 compares the characteristics of SiC to other importance semiconductor materials. The wide bandgap material with the most desirable characteristics is diamond. However, a growth process capable of producing monocrystalline diamond in quantities suitable for semiconductor substrates is not available [2]. It is important to note that the electrical properties stated for SiC extend into the temperature regime much in excess of 300°C which is the approximate upper limit of the operational regime for silicon based devices.

Wide bandgap materials are less subseptible to thermal problems and usually have high breakdown electric fields which allows for increased isolation between devices and higher packing densities. Higher thermal conductivities are also of benefit in enhancing the duty cycle and maximum device packing density. Maximum operating frequencies depend on the saturated drift velocity which is clearly a bonus for SiC. In addition, the lower dielectric constant for SiC increases its value for high frequency device operations.

Table 1. Comparison of Semiconductor Characteristics

PROPERTY	Si	GaAs	GaN	β-SiC (α-SiC)	Diamond
Bandgap (cV) at 300 K	1.1	1.4	3.5	2.3 (>2.9)	5.5
Maximum operating temperature (°C)	300	460	500	873 (1240)	1100 (?)
Melting point (OC)	1420	1238	1700 (600 -	Sublimes >1800	Phase change
Physical stability	Good	Fair	dissociates) Good	Excellent	Very good
Electron mobility	1400	8500	>440	1000 (600)	220Q
(cm ² /V-s) Hole mobility	600	400	not available	40	1600
(cm ² /V-s) Breakdown field, E _b	0.3	0.4		4	10
$(10^{6} { m V/cm})$ Thermal conductivity, σ_{T}	1.5	0.5	1.3	5	20
(W/cm-°C) Saturated electron drift velocity,	1	2		2.5	2.7
v _{sat} (107 cm/s) Dielectric constant, ε	11.8	12.8	12,1	9.7	5.5

The crystal structure of SiC has a one dimensional polymorphism referred to as polytypism [3]. The result is a unique aspect of this material whereby it can exist in a possibly infinite number of crystallographic structures called polytypes. Nearly 200 polytypes have been identified at present. These structures fall into two categories referred to as alpha (α) and beta (β). The α category contains primarily hexagonal, rhombohedral and trigonal structures while the β category contains one cubic or zincblende structure (e.g., see Table 2). The cubic or zincblende structure, referred to

as β -SiC. (3C-SiC), is expected to have the highest electron mobility (1000 cm²/V-s) [2]. The beta form is also a potential substrate for important cubic structured materials such as α -GaN and diamond. The beta polytype, although having the most favorable electrical characteristics, is difficult to grow in a monocrystalline form due to its apparent metastability resulting in a solid state transformation into an alpha structure. Due to the difficulty in the growth of β -SiC., most commercial efforts for producing bulk monocrystalline growth have concentrated on the more easily prepared α polytype, referred to as 6H-SiC. In the area of epitaxial growth of thin films, though, both 3C and 6H-SiC are of considerable commercial interest with both n- and p-type conductivity possible with the addition of the appropriate impurities.

Fig. 1 shows a depiction of the silicon-carbon tetrahedral comprising the beta and alpha silicon carbide structures, The primary difference between the crystal structures arises from a slightly different orientation in the upper and lower overlapping tetrahedrons. In the case of the cubic or zincblende structure the upper and lower atoms are in a staggered position. The corresponding atomic arrangement forming the purely hexagonal alpha structure is an eclipsed one. Each of these structures can also be viewed as composed of two double layers of silicon and carbon atoms wherein the top layer in each structure forms the bottom layer in the structure above it. If the purely cubic or beta (3C) form is viewed along the<111 > direction and the purely hexagonal form (2H) is viewed along the <0001> direction, all the different SiC polytypes are observed to exist as different layered combinations of staggered and eclipsed tetrahedral structures. The 6H-SiC polytype, for example, consists of a six layer repeat pattern of silicon and carbon atoms. These layers can also be viewed as consisting of one eclipsed tetrahedral structure in the middle of four staggered ones (i.e. symmetrically spaced; see fig. 2). The hexagonal alpha forms are composed

Table 2. Silicon Carbide Polytypes.

THIBAULT NOTATION			RAMSDELL NOTATION		
α - SiC			6H 4H 2H		
β - SiC			3C		
Other repo	rted struct	ures (all α	- SiC) -		
8H I OH	16Н 18Н	21R 24H	33R 39R	51R	
	15R	19H	27R	48H	
Plus many	others				
Note: H, C, R refers 10 hex	aganal aul	nia and tho	mhohadral	otenaturas raspastivaly)	

of single eclipsed tetrahedral structures evenly spaced between staggered ones. The rhombohedral structures, in contrast, have single eclipsed tetrahedral structures that are non symmetrically spaced between stacks of staggered tetrahedral structures. The low stacking fault energy arising from the transformation from the staggered to the eclipsed arrangement is believed to result in the observed beta to alpha transformation at elevated temperatures (>1900°C) [4,5].

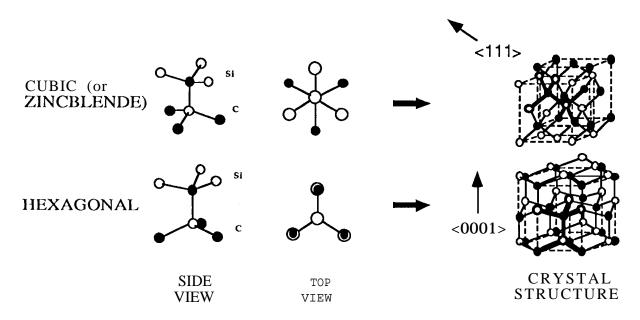
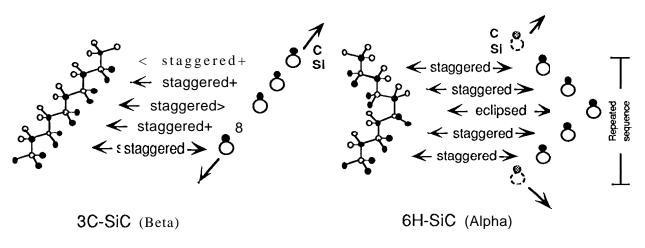


Figure 1. Silicon carbide tetrahedral structures.

MATERIAL GROWTH AND FABRICATION TECHNIQUES

Silicon carbide was produced primarily by the Acheson process for use as an abrasive up until the time of the early work of J. A. Lely in 1955 [6]. The crystal material produced by the Acheson process (2600 - 2700°C) grew in large irregular masses and were almost exclusively of the alpha variety. The Lely process used relatively impure polycrystalline and microcrystalline SiC source crystals prepared by the Acheson method to grow very small, but very good quality single crystal α -SiC platelets, using a sublimation-condensation technique. This technique was implemented at



Crystal Stacking Sequence

Figure 2. Comparison of beta and alpha SiC crystal stacking sequences.

temperat ures near **2600**°C. The appearance of β-SiC. was rare at these temperatures which seemed to favor growth of the alpha variety. This growth process for producing good quality, single crystal SiC remained essentially unchanged until the work of Tairov, *et al.*, in the 1970's [7,8] and later by Vodakov, *et al.* [9]. These efforts, conducted at the Leningrad Electro-Technical Institute and the A. F. Ioffe Physical-Technical Institute in St. Petersburg, Russia Federation, used a modified Lely growth technique, whereby a seed crystal was introduced to provide a compatible surface for nucleation. Most of the research conducted at these institutes involved the growth of single crystal alpha type SiC. Nucleation of both the alpha and beta polytypes, however, were attempted on both Acheson and Lely platelets and on epitaxial layers grown by liquid and vapor phase techniques. The growth temperatures used in these experiments ranged from about 1850°C to that used in the Lely method (i.e. near 2600°C).

Work on the bulk growth of SiC was also proceeding in the United States [10] following the publication of Lely's work in the Federal Republic of Germany. The Lely sublimation growth process was used almost exclusively until recently. Due to difficulties with this process such as the inability to produce controlled nucleation and the occurrence of mixed polytypes, other methods were investigated [11, 12] such as growth from solutions. Interest was rekindled following the first successful use of a seeded growth (modified Lely) sublimation process in the United States [13]. These efforts, however, have concentrated on the growth of primarily two alpha polytypes (6H and 4H).

Rapid developments in both bulk and epitaxial growth technologies occurred during the 1980's. There are now commercially available 2.5 -5 cm diameter SiC wafers (e.g. 4H and 6H-SiC) [14,15]. Material grown rates for bulk single crystal of these two principal forms of alpha SiC vary from about 0.25 to 2 mm/hr. Although no β -SiC. substrates are commercially available, a research program at Howard University has successfully produced the first bulk grown β -SiC. useful for preparing substrates for electronic devices [16, 17, 18], The maximum growth rate for single crystal material achieved is about 130 mm/hr with a 7- 10 mm substrate diameter.

The principal technique for producing thin films of SiC for device layers is by a chemical vapor deposition (CVD) process. CVD on silicon substrates is the principal means of producing β -SiC. thin films due to the lack of commercially available β -SiC. substrates. Epitaxial films have also been successfully prepared using other vapor phase and liquid phase epitaxy techniques [19,20,21]. These processes, though, are capable of producing monocrystalline layers that are of the order of tens of microns in thickness at maximum. In addition, these growth processes are relatively slow (typically less than 3 microns per hour in order to produce single crystal material).

SiC SENSORS AND DEVICES

HIGH TEMPERATURE, POWER, AND FREQUENCY DEVICES

The wide bandgap, high thermal conductivity (-3 times silicon) and melting point of SiC is an advantage for almost any device fabricated from SiC. Beta-SiC has higher n and p-type nobilities than 6H-SiC or any of the other α polytypes due to its simpler crystal structure and is expected to produce faster devices. Most devices being fabricated, however, use 6H-SiC which is presently more available than β-SiC.. The SiC crystal structure is compatible with many high temperature materials (e.g., A IN, GaN, SiO₂, MoC, TiC, TaC, etc.) which makes many devices feasible. JFETs, MESFETs, MOSFETs, and pn junction rectifiers, and storage capacitors (mostly 6H-SiC) have been produced, and high frequency (100 GHz) IMPATT diodes are under development [22,23]. Devices such as pn junction rectifiers have been tested for more than 1000 hrs at 360°C.

MESFETs and JFETs have good measured characteristics to 500°C. Some MOSFETS have very good measured characteristics to 650°C.

A number of areas still require work. High temperature ohmic and rectifying contacts are still undergoing development, Questions exist as to the degradation of contact structural integrity over time at elevated temperatures. A number of proprietary processes exist to increase the stability of the metal - SiC interface. Substrate technology is also still undergoing development. Commercially available 6H-SiC and 4H-SiC wafers are between 1 -1.5 inches in diameter. Two inch wafers are already in limited supply while larger wafers are expected within a couple of years. Substrates composed of β-SiC. should be commercially available within 1 -2 years. Epilavers grown on 6H-SiC and silicon substrates primarily produced by chemical vapor deposition processes are presently used for fabricating devices. In addition, defect densities in both substrates and epilayers need to be reduced to increase device performance. The primary defect in bulk 6H and 4H-SiC, the micropore or micropipe, which extends in the c-axis direction completely through the bulk material, has been reported by commercial sources to have been reduced to about 10 per cm² from nearly 100 per cm² in 1994. Also present SiC devices are limited to simple mesa and planar structures due to more difficult processing techniques than those of semiconductor materials such as silicon. This limitation is changing as fabrication techniques improve.

OPTOELECTRONICS

The wide bandgap of the various SiC crystal structures make them candidates for far UV radiation detection. Commercially available devices include ultraviolet photodetectors and blue and violet light emitting diodes [24]. High temperature photodetectors are also under development, Ultraviolet photodetectors constructed from α -SiC in the form of 6H and 4H-SiC have been used to detect UV radiation in the range 200-400 nm. Ultraviolet enhanced silicon photodiodes, by contrast, do not detect below 300 nm. The detection peak for α -SiC photodiodes is between 200-300 nm, Doping of both α - and β -SiC can potentially be used to shift the detection peak. SiC operates well up to 600- 800°C, while UV detection at high temperatures is not possible with silicon photodiodes or CCDs. Dark current ("noise") for SiC detectors is low; <10-9 A/cm² at 10V and 25°C, and 10-8 A/cm² at 10V and 350°C compared to silicon at 10-7 A/cm² at 10V and 25°C.

Silicon Carbide is also an indirect bandgap material which implies that no SiC lasers are envisioned. Direct bandgap material can easily be achieved, however, from solid solutions of SiC and two other important wide bandgap materials, AIN and GaN, with bandgaps ranging from about 4 to 6 eV with lower values achievable using appropriate acceptor and donor impurities.

Although SiC can not be used as a lasing material, it is a potential waveguide substrate for nitride based optoelectronics. GaN is a potential candidate for a UV semiconductor laser. The nitride family, however, has proven to be very difficult to grow in a single crystal form. SiC has been successfully utilized as a substrate for growth of several desirable nitrides with potential usefulness for UV optoelectronics. Relatively high intensity 500 µm blue LEDs are now commercially available that have been fabricated from GaN grown on the basal plane of 6H-SiC. In addition, composite structures composed of a GaN heterostructure grown on a AIN waveguide which in turn has been grown on a supporting substrate of SiC are expected to provide a variety of promising optoelectronic devices.

GAS, CHEMICAL AND PRESSURE SENSORS

Semiconductor materials such as silicon, have proven to be very useful for pressure and strain sensors due to their large piezoelectric coefficients. The current available operational range of semiconductor pressure sensors is up to about 500°C. There is however a growing demand for sensors capable of operating at temperatures much greater than 500°C for automotive and avionic

applications. SiC is proving to be a promising semiconductor material for such potential applications at high temperatures. SiC is one of the most refractory materials known, and thin membranes of SiC should be very robust while not rigid. And because SiC is a semiconductor material, integration of microsensors, microactuators, and integrated circuits on a common substrate using microfabrication techniques are possible. Although the refractory qualities of SiC make it difficult to machine, photo electrochemical methods have been shown to be an effective etchant and could be used to make thin membranes and structures. A pressure sensor that takes advantage of SiC's thermal indifference and hardness could operate in extreme temperature and pressure conditions, such as inside an engine or turbine. Examples of potential high temperature pressure sensors are; (1) a piezoresistor that can be made from n-type β -SiC and used in strain gauges, (2) a capacitance manometer that could be made from p- and n- type β -SiC.

Relatively new research has been conducted in the area of chemical and gas sensors utilizing SiC. The primary emphasis of these efforts have involved metal-oxide-SiC catalytic structures [25]. Ions arising from hydrogen bearing molecules dissociated on a catalytic metal layer diffuse to the metal -oxide interface. The ions adsorbed at the interface act as a dipole layer, that lowers the flat band voltage of the MOS capacitor structure or vary the depletion layer in a field effect transistor. Molecular species such as hydrogen, hydrogen sulfide and ethanol can be detected with thick, continuous catalytic metal gates on MOS capacitors. Certain reactions, though, such as the dissolution of saturated hydrocarbons occur effectively at temperatures above 350°C. The high temperature required for these reactions made SiC a likely candidate for the semiconductor portion of the MOS structure comprising such gas detectors.

In particular, novel new gas sensors are under investigation at the Caltech Jet Propulsion Laboratory (JPL) in support of NASA's Partnership for a New Generation of Vehicles Program or "Clean Car Initiative" with the major United States automakers. The ability of SiC based electronic device structures to operate at temperatures up to about 800°C allows the material to be used to fabricate effective sensors to monitor hydrocarbons in exhaust streams in internal combustion engines and processing plants and, in combination with suitable electronics, air quality in passenger cabins and work areas. Hydrocarbons, which require temperature in excess of 350°C for effective catalysis, can be adsorbed and dissociated on a catalytic surface supported by SiC. The ionic buildup resulting from the dissociated molecules changes the electrical characteristics of SiC and can also be utilized in the detection of hydrocarbons. Possible catalytic surfaces include SiC itself, thin films of metals (e.g. platinum), and thin films of refractory metal carbides which are resistant to oxidation at temperatures up to 700°C (e.g. WC, MoC, possibly TiC, NbC or alloys). The hydrocarbon gas sensor being developed by JPL, in contrast, makes use of a modified form of SiC referred to as porous SiC. A photoelectrochemical process is used to create a nanoporous layer of SiC. This layer is then used as part of a SiC sensor is which hydrocarbon gas molecules are adsorbed on the large surface area and dissociated by the application of a relatively small potential (i.e. about 4 to 10 volts). Due to the different hydrogen - carbon bond strengths for the various hydrocarbon species there is a slightly different dissociation potential that can be used for discrimination between them [26].

TELECOMMUNICATIONS

Another application involving microstrip antennas has only recently been considered. Microstrip antennas are becoming more and more popular in applications such as space expl oration, and in military, commercial and medical fields. They are low volume, low profile and low mass. These antennas are of particular interest for small and micro-scale spacecraft because of their size and mass, and because they can be made conformal to the spacecraft surface.

The use of silicon carbide (SiC) as a self-supporting antenna material offers the possibility of fabricating a thin, low mass antenna which can operate at temperatures of 500-800 "C. α -SiC is a very rugged, abrasion resistant semiconductor with a band gap -3 eV. It has a low thermal conductivity and low coefficient of thermal expansion, and can be grown either as an insulator or as a highly conductive material. Using SiC as the dielectric and support as well as the transmission material will eliminate any potential for buckling, as there will be no thermal expansion mismatch. The robust nature of SiC also makes it possible to make thin, self-supporting, monolithic antennas, on the order of 350 μ m thick. Thinner substrates are also possible, which can be applied to antennas for THz frequencies.

Transmission lines can be constructed on a conductive SiC substrate by modifying the surface to create i nsul sting regions of porous SiC. SiC may be modified using a direct-write photoelectrochemical technique, in which porous-SiC is made electrochemically under illumination with light more energetic than the band-gap. Processing is done in an aqueous electrolytic etching solution, under atmospheric conditions, using a light source such as a lamp or a 1 aser. The resolution of a photoelectrochemical processing technique is on the order of $0.5~\mu m$; thus an antenna for wavelengths in the hundreds of GHz or THz regime may be constructed using this technique.

SUMMARY

Significant progress has been achieved over the past decade in the crystal growth of wide bandgap semiconductor materials. The most successful material technology is that of SiC. The prospects for device implementation are better for SiC than for any of the other wide bandgap materials. Electronic devices and sensors in the areas of high temperature, high power and frequency that are Fabricated from SiC are now commercially available. The recent production of large area substrates of SiC has made high quality epitaxy possible. As device fabrication techniques continue to improve integrated circuits of significant complexity are expected. The present development efforts have involved extending the operational regime of silicon based electronics and fabrication of sensors, photodiodes, and light emitting diodes that perform in the blue through ultraviolet regions of the spectrum. In addition, SiC materials are now being utilized in areas such as gas sensing and telecommunications. New opportunities exist in these areas that are not as yet developed and others as yet to be determined.

ACKNOWLEDGMENT

This work was supported by **the** Jet Propulsion Laboratory at the California Institute of Technology. The author thanks Drs. Margaret A. Ryan and Roger M. William for some of the information used in the preparation of this manuscript.

REFERENCES

- ¹ J. A. Lely, Ber. Deut. Keram. Ges. 28, 229 (1955).
- ²J H. Edgar, Journal of Material Research 7, 1 (1992).

- N. Jepps and T. Page, in Progress in Crystal Growth and Characterization, Vol. 7- Crystal Growth and Characterization of Polytype Structures, P Krishna. Ed., New York, 1983, Pergamon, Chapter 6, pp. 259-307.
- P, Pirouz, J. W. Yang, J. A. Powell, and F. Ernst, Microsc. Semiconductor Materials Conference, March 1991, Institute of Physics Conference Series No. 117: Section 3, pp. 149-154.
- ⁵ P. Pirouz and J. Yang, Material Research Society Symposium Proceedings 183, 173 (1990).
- W. Knippenburg, Philips Research Report 18, 161 (1963).
- Yu. M. Tairov and V. F. Tsvetkov, Journal of Crystal Growth 43,209 (1978).
- ⁸ Yu. M. Tairov and V. F. Tsvetkov, Journal of Crystal Growth 52, 146 (1981).
- Yu. A. Vodakov, E. N. Mokhov, M. G. Ramm, A. D. Roenkov, Kristall und Technik 14, 729 (1979).
- J. A. Powell and L. G. Matus, Springer Proceedings in Physics, Vol. 34 (Springer, Berlin, Heidelberg, New York, 1989).
- W. E. Nelson, F. A. Halden and A. Rosengreen, Journal of Applied Physics 37,333 (1966).
- ¹² L. B. Griffiths and A. 1. Mlavsky, Journal of Electrochemical Society 111,805 (1964).
- ¹³ C. H. Carter, Jr., L. Tang and R. F. Davis, presented at the Fourth National Review Meeting on the Growth and Characterization of SiC, Raleigh, NC (1987).
- S. Nishino, Y. Kojirna, and J. Saraie, Springer Proceedings in Physics, Vol. 56 (Springer, Berlin, Heidelberg, New York, 1992).
- D. L. Barrett, R. G. Seidensticker, W. Gaida, R. H. Hopkins, and W. J. Choyke, Springer Proceedings in Physics, Vol. 56 (Springer, Berlin, Heidelberg, New York, 1992).
- ¹⁶ V. Shields, K. Fekade, and M. Spencer, Applied Physics Letters 62 (16), 1919 (1993).
- V. Shields, K. Fekade and M. Spencer, Silicon Carbide and Related Materials, Proceedings of the Fifth Conference, Nov. 1993, Institute of Physics Conference Series No. 137: Chapter 1, pp. 21-24,
- ¹⁸ H. Jayatirtha, M. Spencer, V. Shields, 36th Electronic Materials Conference, June 1994.
- G. L. Harris, K. H. Jackson, G. J. Felton, K. R. Osborne, K. Fekade and M. G. Spencer, Material letters 4 (2),77 (1986).
- J. A. Powell and L. G. Matus, Springer Proceedings in Physics, Vol. 43 (Springer, Berlin, Heidelberg, New York, 1989), pp. 14-19.
- K. Irvine, M. Spencer, and M. Aluko, Springer Proceedings in Physics, Vol. 56 (Springer, Berlin, Heidelberg, New York, 1992).
- J. A. Edmond, J. W. Palmour, C. H. Carter, Proceedings of the 1991 International Semiconductor Device Research Symposium, M. Shur, cd., 1991, pp. 487.
- J. A. Edmond, H. S. Kong, C. H. Carter, Proceedings of the 1991 International Semiconductor Device Research Symposium, M. Shur, cd., 1991, pp. 491.
- ²⁴ J. A. Edmond, H. S. Kong, C. H. Carter, Physics B 185, 453 (1993).
- ²⁵ A. Arbab, A. Spetz, I. Lundström, Sensors and Actuators B 15-16, 19 (1993).
- V. Shields, M. Ryan, R. Williams, M. Spencer, D. Collins, D. Zhang, presented at the 6th International Conference on Silicon Carbide and Related Materials, Sept. 1995, Kyoto, Japan).